The maintenance of elevated active chlorine levels in the Antarctic lower stratosphere through HCl null cycles

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The Antarctic ozone hole arises from ozone destruction driven by elevated levels of active chlorine in Antarctic spring. These elevated levels of active chlorine have to be formed first and then maintained throughout the period of ozone destruction. Here we discuss, how this maintenance of active chlorine is brought about in Antarctic spring, when the rate of formation of HCl is extremely high. Here we show that in the heart of the ozone hole (390–430 K, 16–18 km or 85–55 hPa, in the core of the vortex), high levels of active chlorine are maintained by effective chemical cycles (referred to as HCl null cycles hereafter). In these cycles, the formation of HCl is balanced by immediate reactivation, i.e. by immediate reformation of active chlorine. Under these conditions, polar stratospheric clouds sequester HNO_3 and thereby cause NO_2 concentrations to be low. These HCl null cycles allow active chlorine levels to be maintained in the Antarctic lower stratosphere and thus rapid ozone destruction to occur. For the observed almost complete activation of stratospheric chlorine in the lower stratosphere, the heterogeneous reaction $HCl + HOCl$ is essential; the production of HOCl occurs via $HO_2 + ClO$, with the HO_2 resulting from CH_2O photolysis. Further, we find that when the formation of methylhypochlorite in the reaction $ClO + CH_3O_2$ is taken into account, it is important that also the main loss channels for methylhypochlorite (photolysis and reaction with Cl) are considered. Provided that this is the case, there is only a moderate impact of the formation of methylhypochlorite on polar chlorine chemistry. These results are important for assessing the impact of changes of the future stratospheric composition on the recovery of the ozone hole. Our simulations indicate that, in the lower stratosphere, future increased methane concentrations will not lead to enhanced chlorine deactivation (through the reaction $CH_4 + Cl \rightarrow HCl + CH_3$) and that extreme ozone destruction to levels below ≈ 0.1 ppm will occur until mid-century.

Key words: Ozone hole, Antarctic chlorine chemistry, HCl null cycles

References

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